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Scope of Patent Claims

[Claim 1] A method of nitrile preparation comprising reacting an alkane in a gas phase contact reaction with ammonia in the presence of a catalyst conforming to:



(Where in Formula (1), X represents one or more elements selected from Nb, Ta, Ti, Re, Al, Zr, Cr, Mn, Fe, Ru, Co, Rh, Ni, Pd, Pt, Sb, Bi, In or Ce; and when $a = 1$,
 $b = 0.01$ to 1.0
 $c = 0.01$ to 1.0
 $x = 0.01$ to 1.0 , and n is determined by the oxide form of the element.

Details of the Invention

Area of Industrial Application

The present invention relates to a method of nitrile preparation, specifically an improved method of nitrile preparation using alkane raw materials.

Prior Art

Nitriles such as acrylonitrile and methacrylonitrile are manufactured for industrial use as intermediates for fibers, synthetic resins, synthetic rubbers and the like. The most conventional

method for their manufacture was to perform a high temperature gas phase contact reaction using an olefin such as propylene or isobutene with a catalyst and reacting with ammonia and oxygen.

On the other hand, due to the cost differentials between propane and propylene, and between isobutane and isobutene, there was a great deal of interest in developing a process of preparing acrylonitrile or methacrylonitrile using the so-called ammoxidation process, which would react a lower alkane such as propane or isobutane with ammonia and oxygen in the presence of a catalyst.

Examples of reported catalysts include Mo-Bi-P-O catalysts (Japan Patent "Kokai" Application Sho 48-16887, V-Sb-O catalysts (Japan Patent "Kokai" Applications Sho 47-33783 and Hei 1-268668, and Japan Patent Sho 50-23016)), Sb-U-V-Ni-O catalysts (Japan Patent Sho 47-14371), Sb-Sn-O catalysts (Japan Patent Sho 50-28940), V-Sb-W-P-O catalysts (Japan Patent "Kokai" Application Hei 2-95439), V-Sb-W-O catalysts mechanically mixed with Bi-Ce-Mo-W-O catalyst (Japan Patent "Kokai" Application Sho 64-38051), etc. The present inventors have also previously reported an Mo-V-Te-Nb-O catalyst (Japan Patent "Kokai" Application Hei 2-257).

Problems To Be Resolved by this Invention

However, the foregoing methods did not deliver entirely satisfactory yields of the target nitriles. Other methods added small amounts of organic halogen compounds, inorganic halogen compounds or sulfur compounds, or added water as a means of improving nitrile yields, but the former caused corrosion problems and the latter produced byproducts from side reactions that necessitated further processing; as a result, neither approach was practical for industrial scale production.

Further, with the exceptions of the prior art method by the present inventors using the Mo-V-Te-Nb-O catalyst and a few other examples, the reaction temperature had to be very high, at around 500°C, and such high temperatures were disadvantageous from the perspective of requiring special materials for equipment that increased production costs.

Means Used To Resolve Problems

As a result of exhaustive evaluation of methods to produce nitriles using alkane starting materials by the present inventors, we discovered that in the presence of a catalyst comprise of tungsten (W), vanadium (V), tellurium (Te) and a metal selected from a specific list, that it was possible to carry out a gas phase contact reaction between an alkane and ammonia at a relatively low temperature of 400-470°C and obtain higher yields of nitriles than could be obtained in the prior art -- this, without addition of halogen compounds or water to the reaction system.

To wit, the gist of the present invention is a method of nitrile preparation comprising reacting an alkane in a gas phase contact reaction with ammonia in the presence of a catalyst conforming to:



(Where in Formula (1), X represents one or more elements selected from Nb, Ta, Ti, Re, Al, Zr, Cr, Mn, Fe, Ru, Co, Rh, Ni, Pd, Pt, Sb, Bi, In or Ce; and when a = 1, b = 0.01 to 1.0, c = 0.01 to 1.0, x = 0.01 to 1.0, and n is determined by the oxide form of the element.

The invention will be explained in further detail below. The catalyst used in this invention is the compound oxide compound expressed by the foregoing formula (1). While all of the aforementioned elements can be used as the X, preferred examples feature selections from Nb, Ta, Ti and Re, with the use of Nb being especially preferred. Regarding the coefficients in Formula (1), when a = 1, the preferred ranges are b = 0.1 to 0.6, c = 0.05 to 0.6 and x = 0.01 to 0.4.

The foregoing catalyst may be prepared as follows. For the case of a catalyst conforming to $W_a V_b Te_c Nb_x O_n$, the required amount of ammonium metatungstenate is dissolved in water and addition is then made of an aqueous solution of telluric acid, and aqueous solution of niobuammonium oxalate, and an aqueous solution of ammonium paramolybdate in amounts that would provide the desired weights and atomic ratios among the metal elements. The evaporative drying method, the spray drying method, vacuum drying method, etc. may then be used to dry

the solution, and then the remaining dried substance can be baked to obtain the desired oxide. It is also possible to heat the residuals in air or in a nitrogen, argon or other inactive gas environment to 150 to 350°C prior to the final drying in order to facilitate the drying process.

The baking process is most usually conducted in an oxygen environment, but conversely, with regard to catalysts according to this invention, it is best to perform the baking in a virtually oxygen free environment, in an environment that contains nitrogen, argon, helium or other inactive gas; or one which contains such a gas in addition to a hydrocarbon reducing agent or water vapor; or in a vacuum. The baking is normally performed at 350 to 700°C, preferably 400 to 650°C for from 0.5 to 30 hours, preferably from 1 to 10 hours.

Also, the catalyst is not confined to being prepared from the foregoing starting materials; they may be selected from a broad range of oxides such as WO_3 , V_2O_5 , V_2O_3 , TeO_2 , Nb_2O_5 , etc.; halogen or oxyhalogen compounds such as WCl_3 , VOCl_3 , NbCl_3 , etc.; or alkoxy compounds such as $\text{VO}(\text{OEt})_3$, $\text{Nb}(\text{OEt})_3$, etc.

The foregoing catalyst may be used by itself, but it is also possible to use it on a conventional catalytic support such as silica, alumina, titania, aluminosilicate, diatomaceous earth, etc. The shape and particle size of the catalyst may be determined appropriately according to the scale and method used to perform the reaction. Under this invention and in the presence of the above described catalysts, it is possible produce nitriles in a highly efficient manner using a gas phase contact reaction between an alkane and ammonia.

This invention imposes no especial restrictions upon the alkane starting materials used to prepare the nitriles. Examples include methane, ethane, propane, n-butane, isobutane, pentane, hexane, heptane, cyclohexane, etc., but when considering industrial scale production of nitriles, the lower alkanes with 1 to 4 carbon atoms, especially the use of propane or isobutane is preferred.

While the details of the mechanism of the oxidation reaction that takes place during this invention are not entirely clear, it can take place using the oxygen atoms that exist in the oxides used, or using molecular oxygen present in the gas supply. In cases where oxygen is present in

the gas supply, pure oxygen may be used, but it is more economical to use an oxygen-containing gas such as air. Generally a gas mixture containing argon, ammonia and an oxygen-containing gas would be supplied to the reaction as a gas mixture, but it is also possible to alternate between the types of gas supplied.

It is further possible to supply just argon and ammonia without any presence of molecular oxygen in performing the gas phase contact reaction. In this case, oxygen would be appropriately drawn off the catalyst in the reaction, and then the catalyst could be rejuvenated and reused. An example of a catalyst rejuvenation method is to pass oxygen or air over the catalyst in a catalyst rejuvenation vessel at a temperature of 300 to 600°C.

To explain this invention in even more detail for the case where the alkane is propane and air is used as the oxygen source, the amount of oxygen supplied to the reaction has an important effect on the selectivity for the nitriles being produced. Normally, the amount of air should be 25 moles per mole of propane or lower, preferably in a range of 1 to 15 moles of air, which makes it possible to obtain a high acrylonitrile selectivity. The ratio of the ammonia used in the reaction should be 0.2 to 5 moles per mole of propane, preferably 0.5 to 3 moles. This reaction would normally be conducted at atmospheric pressure, but it will also take place under slightly pressurized or vacuum conditions. The composition of the gases supplied for other types of alkanes may be computed based upon the conditions for propane.

The method of this invention provides a lower reaction temperature compared with prior art ammoxidation reactions of alkanes, for example, it can be implemented at 340 to 480°C, preferably between 400 and 470°C./ The spatial velocity (SV) of the gases in the gas phase reaction should normally range between 100 and 10000h⁻¹, preferably between 300 and 200h⁻¹. Nitrogen, argon, helium or other inactive gas may be used to adjust the spatial velocity and the partial pressure of the oxygen.

Examples

Examples and Comparative Examples of this invention will be used for further explanation, but the invention is not confined to these examples. In the Examples and

Comparative Examples, the following formulas were used to calculate the conversion rate (%), the selectivity (%) and the yield (%).

$$\text{alkane conversion rate (\%)} = (\text{moles of alkane consumed} / \text{moles of alkane supplied}) \times 100$$

$$\text{nitrile selectivity (\%)} = (\text{moles of nitrile produced} / \text{moles of alkane consumed}) \times 100$$

$$\text{nitrile yield (\%)} = (\text{moles of nitrile produced} / \text{moles of alkane supplied}) \times 100$$

Example 1

A catalyst having the formula of $W_1V_{0.3}Te_{0.23}Nb_{0.12}O_n$ was prepared as follows. 23.2 g of ammonium metatungstenate having 50% by weight of WO_3 was added to 50 g of water, and then 1.75 g of ammonium metavanadate and 2.64 g of telluric acid were added to prepare a uniform aqueous solution. Then, addition was made of 12 ml of a niobioammonium oxylate solution to bring the niobium concentration to 0.5 mol/l in the resulting slurry. The slurry was evaporation dried at about 150°C to obtain a dry residue. The residue was then formed into 7 mm ϕ \times 4 mm L tablets using a tablet forming machine, and then the tablets were crushed and passed through a 16-20 mesh screen before baking for 2 hours at 600°C under a nitrogen flow.

The reaction vessel was filled with 0.5 ml of the resulting catalyst, and then a mixed gas of propane : ammonium : air = 1 : 1.2 : 1.5 was supplied at a fixed spatial velocity (SV) of 500 h⁻¹ at a reaction temperature of 450°C. The results appear in Table 1.

Table 1

	Catalyst Composition	Reaction Temp. (°C)	Propane conversion (%)	Acrylonitrile selectivity (%)	Acrylonitrile yield (%)
Example 1	$W_1V_{0.3}Te_{0.23}Nb_{0.12}O_n$	450	68.8	22.4	15.4
Example 2	$W_1V_{0.3}Te_{0.3}Nb_{0.12}O_n$	460	55.6	26.1	14.5
Example 3	$W_1V_{0.4}Te_{0.2}Nb_{0.1}O_n$	440	53.9	18.6	10.0
Comp. Ex. 1	$V_{0.3}Te_{0.23}Nb_{0.12}O_n$	430	1.8	0	0
Comp. Ex. 2	$W_1Te_{0.23}Nb_{0.12}O_n$	460	0	0	0
Comp. Ex. 3	$W_1V_{0.3}Nb_{0.12}O_n$	400	59.4	2.0	1.2

Comp. Ex. 4	$W_1V_{0.3}Te_{0.23}O_n$	420	12.3	15.0	1.8
Comp. Ex. 5	$Ti_1V_{0.3}Te_{0.23}Nb_{0.12}O_n$	400	63.4	0	0
Comp. Ex. 6	$Zr_1V_{0.3}Te_{0.23}Nb_{0.12}O_n$	400	62.3	0	0
Comp. Ex. 7	$Sn_1V_{0.3}Te_{0.23}Nb_{0.12}O_n$	400	11.3	12.0	1.4

Example 2

The same method was used as in Example 1 but with $W_1V_{0.3}Te_{0.23}Nb_{0.12}O_n$ as the catalyst and with a reaction temperature 460°C. The results appear in Table 1.

Example 3

The same method was used as in Example 1 but with $W_1V_{0.4}Te_{0.2}Nb_{0.1}O_n$ as the catalyst and with a reaction temperature 440°C. The results appear in Table 1.

Comparative Examples 1 through 4

The compound oxide catalysts were prepared as in Example 1 but leaving out one element of W, V, Te, and Nb, respectively, as well as setting the appropriate reaction temperature for each catalyst. The results appear in Table 1.

Comparative Examples 5 through 7

The compound oxides were prepared as in Example 1 but with Ti, Zr, and Sn respectively

substituted for the W component, as well as setting the appropriate reaction temperature for each catalyst. The results appear in Table 1.

Effects of the Invention

This invention's use of a novel catalyst makes it possible to achieve the objective of efficient production of nitriles using alkanes as the raw materials, and it does so without the presence of halogen compounds or water in the reaction, and at a comparatively low baking temperature of 400 to 470°C.

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